

TOPIC 07 – EQUILIBRIUM

7.2: POSITION OF EQUILIBRIUM AND LE CHATLIER'S PRINCIPLE

IB Chemistry

T07D02



7.2 **7.2 The position of equilibrium - 4 hours**

- 7.2.1 Deduce the equilibrium constant expression (K_c) from the equation for a homogeneous reaction. (3)
- 7.2.2 Deduce the extent of a reaction from the magnitude of the equilibrium constant. (3)
- 7.2.3 Apply Le Chatelier's principle to predict the qualitative effects of changes of temperature, pressure and concentration on the position of equilibrium and on the value of the equilibrium constant. (2)
- 7.2.4 State and explain the effect of a catalyst on an equilibrium reaction. (3)
- 7.2.5 Apply the concepts of kinetics and equilibrium to industrial processes. (2)



7.1 – Summation of last class

- Dynamic Equilibrium is in a closed system, no loss or gain of material
- Amounts of reactants and products remain constant
- Dynamic, not static equilibrium. They undergo both forward and reverse reactions
- The rates of forward & reverse reactions are equal
- Equilibrium can be achieved from either direction (starting with the left or right side of the equation)
- We will study reactions in homogeneous equilibria, meaning they are all in the same physical phase.



7.2.1 – Equilibrium Constant (K_c)

- 7.2.1 Deduce the equilibrium constant expression (K_c) from the equation for a homogeneous reaction. (3)
- The position of the equilibrium for a particular reversible reaction can be defined by a constant, K_c
- For the general reaction:
 - $aA + bB \rightleftharpoons cC + dD$

Products on top

'powers' are coefficients

Multiple materials are multiplied

[brackets] = conc mol dm⁻³



7.2.1 – Equilibrium Law

- K_c is for a given temperature, if the temperature changes then the value of K_c does as well
- The general expression of K_c is known as the **equilibrium law** which can be adapted to particular equations to be studied in equilibrium



7.2.1 – K_c Example with Ammonia



	$[\text{N}_2] \text{ (M)}$	$[\text{H}_2] \text{ (M)}$	$[\text{NH}_3] \text{ (M)}$
Ex. 1	0.992	0.763	0.157
Ex. 2	0.299	1.197	0.203
Ex. 3	2.59	2.77	1.82

■ From Table:

▪ Find K_c for each

▪ Exp. 1

▪ Exp. 2

▪ Exp. 3



7.2.1 – K_c for Reversible Reactions

- For the forward reaction:



- For the reverse reaction:



- — or K_c^{-1}



7.2.1 – K_c from either side

- A series of experiments @ 700°C returns a value of K_c of 54 regardless of the starting point of reaction or initial concentrations
- $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$

	$[\text{H}_2] (10^{-3} \text{ M})$	$[\text{I}_2] (10^{-3} \text{ M})$	$[\text{HI}] (10^{-3} \text{ M})$	K_c
Ex. 1	4.56	0.74	13.49	54
Ex. 2	3.56	1.25	15.50	54
Ex. 3	2.25	2.34	16.86	54

- $2\text{HI}(\text{g}) \rightleftharpoons \text{H}_2(\text{g}) + \text{I}_2(\text{g})$

	$[\text{H}_2] (10^{-3} \text{ M})$	$[\text{I}_2] (10^{-3} \text{ M})$	$[\text{HI}] (10^{-3} \text{ M})$	K_c'	$K_c(1/K_c')$
Ex. 1	0.48	0.48	3.52	0.0186	54
Ex. 2	0.50	0.50	3.67	0.0186	54

7.2.1 - Practice

- Write the equilibrium Expression for the following reversible reactions. Each are homogeneous equilibria
 - $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$
 - $\text{Fe}^{3+}(\text{aq}) + \text{SCN}^{-}(\text{aq}) \rightleftharpoons [\text{Fe}(\text{SCN})]^{2+}$
 - $4\text{NH}_3(\text{g}) + 5\text{O}_2(\text{g}) \rightleftharpoons 4\text{NO}(\text{g}) + 6\text{H}_2\text{O}(\text{g})$



7.2.1 – Calculate reverse K_c

- The following reaction is an esterification reaction producing ethyl ethanoate:



- The value of K_c for this reaction is 4.0 @ 25°C
- This equilibrium can be approached from the reverse reaction, find the K_c of that reaction:



7.2.2 – Meaning of the Magnitude of K_c

- 7.2.2 Deduce the extent of a reaction from the magnitude of the equilibrium constant. (3)
- The magnitude of K_c gives us an indication of how far a reaction has gone towards completion under the given conditions
- If K_c is high = equilibrium “lies to the right”
 - $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons 2\text{HCl}(\text{g}) \quad K_c = 10^{18} \text{ @ } 277^\circ\text{C}$
- If K_c is low = equilibrium “lies to the left”
 - $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g}) \quad K_c = 2 \text{ @ } 277^\circ\text{C}$
 - Bonding in HI is weaker than in HCl. HCl doesn't readily decompose in heat, where HI does.
 - Reaction to form HCl goes virtually to completion



7.2.2 – Relative K_c values

- As a general rule:
 - If $K_c \gg 1$ then the reaction is said to go to completion
 - If $K_c \ll 1$ then the reaction has hardly taken place at all
 - The equilibrium constant indicates the extent of a reaction at a particular temperature.
 - It gives no indication of how fast equilibrium is achieved.

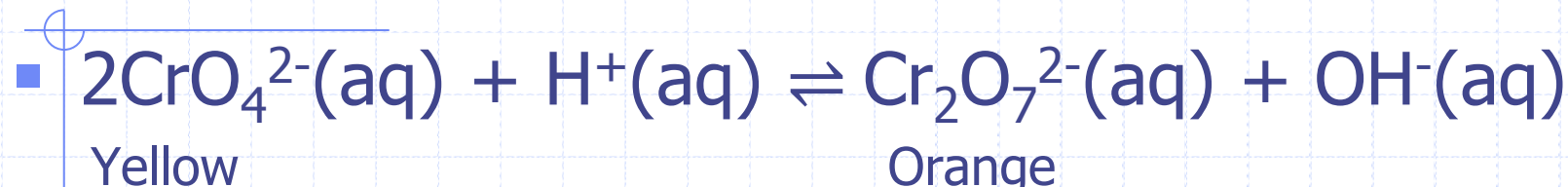
Reaction hardly goes	"Reactants" dominate at Equilibrium	Reactants equal Products	"Products" dominate at Equilibrium	Reaction virtually goes to completion
$K_c < 10^{-10}$	$K_c = 0.01$	$K_c = 1$	$K_c = 100$	$K_c > 10^{10}$

7.2.2 – Alterations to K_c

- K_c is **NOT** altered by:
 - The addition of more reactants
 - The removal of some products
 - Any other adjustment
- Remember, it's the concentration, not the amount
 - If you take away 0.100L of 1.00L solution of 2.0M NaOH, you still have 2.0M NaOH left, just in less volume
- The K_c for a given reversible reaction at equilibrium only changes if the temperature changes



7.2.2 – Chromate and Dichromate



- The shifts are easily seen by a change in color of the ions involved
- Potassium (VI) dichromate is yellow when dissolved
 - Addition of acid pushes reaction to the left to start off at equilibrium, further H^+ pushes the reaction to the right
- Potassium (VI) chromate is orange when dissolved
 - This solution favors a solution of low pH



7.2.3 – Le Chatelier's Principle

- 7.2.3 Apply Le Chatelier's principle to predict the qualitative effects of changes of temperature, pressure and concentration on the position of equilibrium and on the value of the equilibrium constant. (2)
- **"When a system at equilibrium is disturbed, the equilibrium position will shift in the direction which tends to minimize, or counteract, the effect of disturbance."**
-Henri Louis Le Chatelier (1850-1936)



7.2.3 – What does it mean?

- If conditions at which equilibrium have been established change, the position of equilibrium is effected.
- Le Chatelier's principal describes what happens when the dynamic equilibrium is disturbed but does not explain why
 - The system responds to negate the change
 - If more reactant is added, the system will react to remove it
 - If product is taken away, the system will act to replace it



7.2.3 – Effects on position and K_c

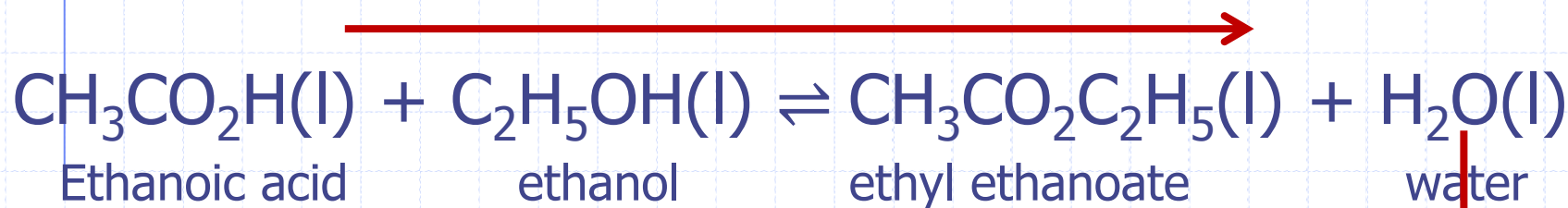
- Possible changes in conditions to consider:
 - Changes in [conc] of reactants or products
 - Changes in pressure for gas phase reactions
 - Changes in temperature
 - The presence of a catalyst

Change Made	Effect on 'position of equilibrium'	Value of K_c
[conc] of one of the components in the mixture	Changes	Remains unchanged
Pressure	Changes if the reaction involves a change in the total # of gas particles	Remains unchanged
Temperature	Changes	Changes
Use of a catalyst	No change	Remains unchanged

7.2.3 – Changes in [conc]

- Again, consider the esterification reaction:

Step 2: equilibrium is shifted to the right



Step 1: Product is removed

- If we remove water, then more of the reactants will react to replace it, producing more ester and water

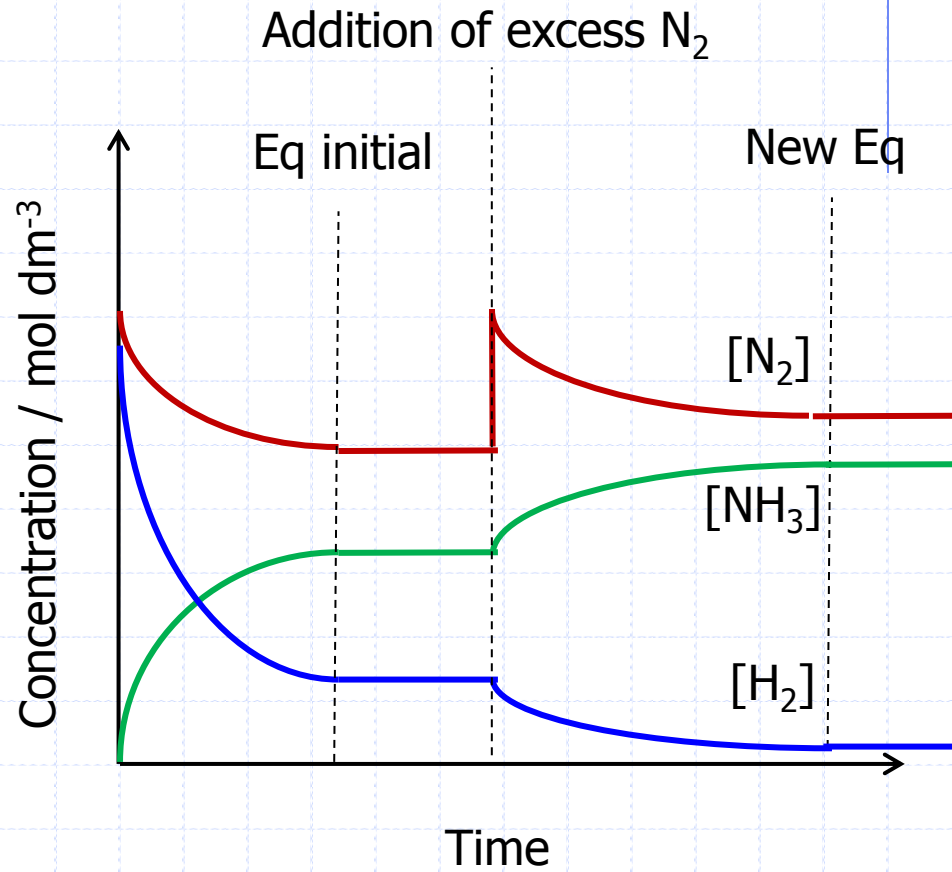
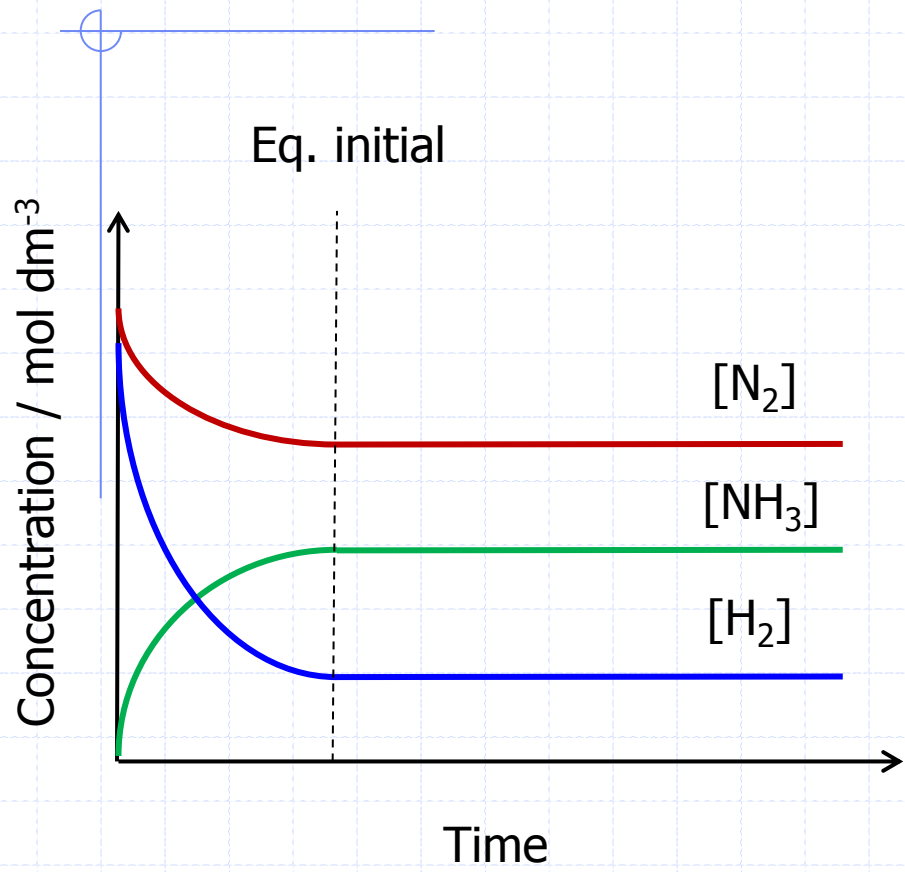


7.2.3 – Production of Ammonia

- A very important industrial process is the production of ammonia (NH_3)
 - $\text{N}_2(\text{g}) + \text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$
 - When the reaction is in dynamic equilibrium, the concentrations are constant
 - If excess $\text{N}_2(\text{g})$ is added, the equilibrium at first is no longer stable
 - To return to equilibrium, more NH_3 is produced
 - Check out the following graphs on the next slide



7.2.3 – Equilibrium Shift for NH_3 production with addition of reactant



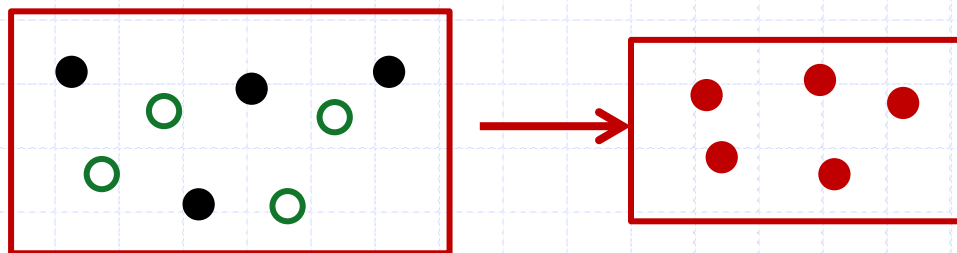
In general:

- Increasing [reactant] shifts equilibrium to the right
- Increasing [product] shifts equilibrium to the left



7.2.3 – Change in Pressure

- Pressure only affects gaseous reactions
- There is a direct relationship between the number of molecules of gas present and the pressure it exerts on its container
- If pressure is increased, the system will favor the side of the reaction with less molecules
 - In doing so the pressure of the mixture will be reduced



Yes, this is a change volume, but in effect it's a change in pressure



7.2.3 – Pressure of N₂O₄

- Useful reaction to study for change in pressure:



colorless

brown

- The equilibrium can easily be monitored by a change in color
- Pressure is increased:
 - Initially darkens the solution, then equilibrium shifts to the left (less molecules) and becomes lighter
- Pressure is decreased:
 - Initially lightens the solution, then equilibrium shifts to the right (more molecules) and becomes darker



This can be demonstrated with a simple syringe

7.2.3 – Change in Temperature

- Consider whether ΔH of the forward reaction is positive or negative
- A reversible reaction has a enthalpy change equal and opposite for each direction (forward and reverse)
- When temperature is increased, the equilibrium position will shift in the direction that will tend to lower the temperature (endothermic direction)
- When the temperature is decreased, shifts toward the exothermic direction



7.2.3 – Effect of Temp on $\text{N}_2\text{O}_4(\text{g})$

- For the same reaction:



colorless

brown

$$\Delta H = + 57 \text{ kJ mol}^{-1}$$

- Decomposition is endothermic
 - If put in an ice bath, color will get lighter
 - If put in a hot water bath, color will get darker

Nature of forward reaction (sign of ΔH)	Change in temperature	Shift in the position of equilibrium	Effect on value of K_c
$\Delta H > 0$	Increase	To the right	K_c increases
$\Delta H > 0$	Decrease	To the left	K_c decreases
$\Delta H < 0$	Increase	To the right	K_c decreases
$\Delta H < 0$	Decrease	To the left	K_c increases

Next Class... Read up 😊

- 7.2.4 State and explain the effect of a catalyst on an equilibrium reaction. (3)
- 7.2.5 Apply the concepts of kinetics and equilibrium to industrial processes. (2)

